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(54) **Preparation of elastomeric, chlorinated ethylene polymers.**

(57) A process of modifying ethylene polymers by reacting granular ethylene polymers having a density of about 0.87 to about 0.92 gram per cc and a pore volume of about 0.1 to about 1 cc per gram with a gaseous chlorinating agent to produce elastomeric, granular, chlorinated polymers having a tensile modulus of less than about 2,000 psi and a crystallinity of less than about 10 percent.

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SUMMARY OF THE INVENTION

This invention relates to the modification of ethylene polymers by reacting, in the absence of solvent or diluent, a granular ethylene polymer, having a density of about 0.87 to about 0.92 gram per cc and a pore volume of about 0.1 to about 1 cc per gram with a gaseous chlorinating agent to produce an elastomeric, granular, chlorinated polymer having a tensile modulus of less than about 2,000 psi and a crystallinity of less than about 10 percent. The elastomeric polymers so produced can be cured to crosslinked products which are useful in the production of film material, as extrudates about wires and cables, as the base polymers in flame retardant compositions and as plasticizers for polyvinyl chloride polymers.

BACKGROUND OF THE INVENTION

Elastomeric, chlorinated ethylene polymers are commercially attractive, as once cured to crosslinked products, they are characterized by a number of desirable properties, including (a) resistance to chemical solvents (b) resistance to ozone (c) resistance to abrasion (d) resistance to outdoor weathering and (e) by excellent use temperatures, i.e. flexibility over a temperature range of about -20°C to about 120°C. Consequently, cured chlorinated ethylene polymers and compositions based thereon, characterized by the properties described above, find uses in many diverse applications including production of film material, as extrudates about wires and cables, as base polymers in flame retardant compositions and as plasticizers for polyvinylchloride polymers.

The preparation of chlorinated ethylene polymers has been carried out, in the past, by a solution process wherein the polymers have been reacted with a chlorinating agent, while in a solvent medium. The so-called solution process requires that the solvent be removed from the chlorinated polymers at the completion of the reaction, generally by heating the reacted system at temperatures sufficiently high to drive off the solvent. At the temperatures employed for solvent removal, however, the chlorinated polymers tend to agglomerate and become difficult to handle and process.

DESCRIPTION OF THE INVENTION

The present invention provides for the chlorination of ethylene polymers by a process which avoids the use of solvents and diluents and their attendant disadvantages and results in the production of granular, elastomeric ethylene polymers which have been homogeneously chlorinated, as evidenced by

an excellent balance of properties. Also, by reason of their granular nature, the chlorinated ethylene polymers of this invention are easy to handle and process.

The results of the present invention are achieved by reacting, in the absence of diluents and/or solvents, a gaseous chlorinating agent with a granular ethylene polymer having a density of about 0.87 to about 0.92 gram per cc, preferably a density of about 0.89 to about 0.91 gram per cc and a pore volume of about 0.1 to about 1 cc per gram, generally about 0.1 to about 0.5 cc per gram and preferably about 0.2 to about 0.4 cc per gram to produce a granular, elastomeric, chlorinated polymer, that is a chlorinated polymer having a tensile modulus of less than about 2,000 psi and a crystallinity of less than about 10 percent.

The chlorinated ethylene polymers so produced, being homogeneously chlorinated and "elastomeric" are characterized by an excellent balance of properties, comparable to commercially available, chlorinated ethylene polymers prepared in an aqueous dispersion.

Ethylene polymers suitable for purposes of the present invention, having the density and pore volume previously described, are ethylene-C_3 to C_8 alpha olefin polymers produced by reacting ethylene with at least one alpha monoolefin under low pressures as further described in U.S. Patent 4,302,565 to George L. Goeke et al patented November 24, 1981, and in application Serial No. 480,296 filed March 29, 1983 assigned to a common assignee.

Particularly desirable ethylene polymers for purposes of the present invention have the density and pore volume described and contain about 50 to about 99 and preferably about 75 to about 96 mole percent ethylene; and about 1 to about 50, preferably about 4 to about 25 mole percent of at least one C_3 to C_8 alpha monoolefin such as propylene, butene-1, pentene-1, 4-methylpentene-1, hexene-1, heptene-1 and octene-1.

Even more desirable ethylene polymers to be chlorinated according to the present invention have:

an average particle size of about 200 to about 1,500, preferably about 300 to about 1,000 microns,

a bulk density of about 10 to about 30, preferably about 15 to about 24,

a pore volume (porosity) of about 0.1 to about 1, generally about 0.1 to about 0.5, and preferably about 0.2 to about 0.4, cc/gm, and

a density of about 0.87 to about 0.92, preferably about 0.89 to about 0.91, gram/cc.

The time of treatment with gaseous chlorinating agent is sufficient to obtain a chlorinated ethylene polymer having a tensile modulus of less than about 2,000 psi and a crystallinity of less than about 10 percent, preferably a crystallinity of 0 to about 5 percent and generally having a total chlorine content of about 5 to about 55 percent by weight, preferably about 15 to about 40 percent by weight.

This treatment is believed to result in the replacement of hydrogen atoms on the backbone of the ethylene polymers with Cl groups.

The actual time of treatment generally varies from about 3 to about 10 hours, depending upon the particular ethylene polymer being chlorinated, the chlorinating agent being used and the temperature and pressure being employed.

Generally, suitable temperatures are in the range of about 50°C to about 130°C, preferably about 50°C to about 100°C. The pressure under which the reaction is conducted can range from atmospheric pressure to a pressure of about 1,000 psi, provided that none of the reactants or by-products condense under the reaction conditions employed. As a rule, the higher the temperature and pressure, the shorter the reaction time.

In carrying out the reaction, the amount of chlorinating agent used is about 10 to about 200 percent by weight, preferably about 20 to about 100 percent by weight based on the weight of the ethylene polymer being treated.

If desired, an inert gas such as nitrogen may be used in conjunction with the gaseous modifying agent, serving as a fluidizing agent, a diffusion aid and/or as a heat sink.

The properties noted herein were determined by the following test methods:

Density (gram/cc)	ASTM-D-1505 - A plaque was made and conditioned for one hour at 100°C to approach equilibrium crystallinity. Measurement for density was then made in a density gradient column.
Pore Volume (cc/gram)	ASTM C-699-108 (45)
Average Particle Size (microns)	Calculated from sieve analysis data measured according to ASTM-D-1921 Method A, using a 500 gram sample. Calculations were based on weight fractions retained on the screens.
Bulk Density	Polymer was poured via 3/8 diameter funnel into a 100 ml. graduated cylinder to the 100 ml. line without shaking the cylinder. Bulk density was determined based on the difference in weight between the unfilled cylinder and the filled cylinder.
Crystallinity (percent)	Measured by Differential Scanning Calorimeter (DSC) using a duPont-990 analyzer with a pressure DSC cell.

Tensile Modulus (psi)	A film, 4 inches by 4 inches by 0.020 inch, was compression molded at a temperature of 130°C - 150°C and its one percent secant modulus measured according to ASTM-D-638.
Tensile Strength (psi)	A film, prepared as described for the Tensile Modulus Test, was tested according to ASTM-D-638.
Percent Elongation at Break	A film, prepared as described for the Tensile Modulus Test, was tested according to ASTM-D-638.

The following Examples are provided to illustrate the present invention and are not intended to limit the scope thereof.

Unless otherwise indicated, the ethylene polymers used as the starting materials in the Examples were prepared by the process disclosed in U.S. application Serial No. 480,296, filed March 29, 1983, assigned to a common assignee, the disclosure of which is incorporated herein by reference.

Apparatus/Process

The ethylene polymers were chlorinated in a two liter glass lined stainless steel or Hastelloy (55% Ni, 17% Mo, 16% Cr, 6% Fe and 4% W) reactor equipped with a thermocouple and a motor activated U-shaped Hastelloy stirrer.

A Hastelloy dip tube (~2 cm in diameter) was used to feed the gaseous modifying agent into the reactor. Unreacted modifying agent and HCl were vented to a collection trap containing 25 percent aqueous NaOH. The gaseous modifying agent was fed at the rate of 8 to 15 grams/hour for Cl_2 under a pressure of about 15 to about 450 psi. The polymer to be treated, about 200 to about 1,000 grams, was charged to the reactor and heated therein

by an external heater. No catalysts were used in carrying out these examples.

After the polymer was added to the reactor and heated to the desired reaction temperature, the polymer was agitated by the stirrer and the gaseous modifying agent was fed in. During the course of the modifying process, samples of the modified polymers were taken from the reactor and tested for chlorine content and percent crystallinity. At the completion of the reaction, the flow of gaseous modifying agent was terminated and the product was allowed to cool in the reactor while the reaction vessel was purged with nitrogen to remove unreacted Cl_2 and HCl by-product.

Three granular, low density ethylene-butene-1 copolymers, A, B and Control 1, having the properties noted below, were chlorinated with gaseous chlorine.

	Control 1	A	B
Density, gm/cc	0.926	0.918	0.875
Mole, percent butene-1 in copolymer	2.4	3.8	20
Crystallinity, percent	50	44	13
Particle size, microns (average)	400	500	400
Porosity, cc/gm	0.3	0.35	0.37
Bulk Density	27	26	21
Tensile Modulus, psi	45,300	36,300	1,160
Tensile Strength, psi	2,190	3,540	290
Elongation, percent	460	983	920

The ethylene-butene-1 copolymers were chlorinated by reaction with gaseous Cl_2 for about 8 to 14 hours at a temperature of 70°C to 80°C for Control 1 and Polymer A and at a temperature of 60°C for Polymer B, to produce chlorinated polymers having properties set forth in Table I.

TABLE I

	Control 1	Control 2*	Example 1	Example 2
Chlorine, percent	24	36	33	20
Crystallinity, percent	5	7.2	2.8	6.5
Tensile Modulus, psi	2,730	930	650	370
Tensile Strength, psi	660	1,110	590	218
Elongation, percent	930	763	900	1,300

* Commercial chlorinated polyethylene available from Dow Chemical Co.

The chlorinated polymer of Control 1 was not elastomeric as evidenced by its "high" modulus. Also, data indicate that the elastomers produced in accordance with this invention have properties comparable to a commercially available chlorinated polymer.

In order to further demonstrate the necessity of utilizing an ethylene polymer having the density and pore volume previously described, Control 3 was carried out using a granular ethylene homopolymer having the following properties:

Density, gm/cc	0.968
Crystallinity, percent	89
Particle size, microns (average)	0.3
Pore Volume, cc/gm	0.3
Bulk Density	27

This copolymer was chlorinated with gaseous chlorine at a temperature of 85°C to 90°C to produce a chlorinated polymer having the properties set forth below.

	Starting Polymer	Intermediate Product	Final Product
Chlorine, percent by weight	0	15	40 (after 30 hrs)
Crystallinity, percent	89	62	35
Tensile Modulus, psi	139,000	94,700	170,000
Tensile Strength, psi	3,470	1,900	3,270
Elongation at break, percent	420	13	2.7

The data of Control 3 indicate that even though the chlorinated polymer had a relatively high chlorine content, it was not elastomeric.

Control 4 was carried out using a granular ethylene-butene-1 copolymer having the following properties:

Density, gm/cc	0.935
Mole % butene-1 in copolymer	1.5
Crystallinity, percent	56.5
Particle size, microns (average)	500
Pore Volume, cc/gm	0.35
Bulk Density	26

This copolymer was chlorinated with gaseous chlorine at a temperature of 90°C to produce a chlorinated polymer having the properties set forth below.

	Starting Polymer	Intermediate Products			Final Product
Chlorine, percent by weight	0	11	17	25	30
Crystallinity, percent	56.5	32	32	34	29
Tensile Modulus, psi	61,600	20,200	37,100	57,100	83,900
Tensile Strength, psi	2,670	1,900	1,980	2,810	2,720
Elongation at break, percent	85	75	36	52	19

The data of Control 4 indicate that even though the chlorinated polymer had a relatively high chlorine content, it was not elastomeric.

The polymers of Controls 1,3,4 and polymer A were prepared according to the process disclosed in U.S. Patent 4,302,565.

Chlorinated ethylene polymers of this invention can be peroxide cured to crosslinked products using peroxides such as di-α-cumyl peroxide as is well known in the art.

WHAT IS CLAIMED IS:

1. A process of chlorinating an ethylene polymer which comprises reacting a granular ethylene polymer having a density of about 0.87 to about 0.92 gram per cc and a pore volume of about 0.1 to about 1 cc per gram with a gaseous chlorinating agent to produce an elastomeric, granular, chlorinated ethylene polymer having a tensile modulus of less than about 2,000 psi and a crystallinity of less than about 10 percent.

2. A process of chlorinating an ethylene polymer which comprises reacting a granular ethylene-C_3 to C_8 alpha olefin polymer having a density of about 0.87 to about 0.92 gram per cc and a pore volume of about 0.1 to about 0.5 cc per gram with a gaseous chlorinating agent to produce an elastomeric, granular, chlorinated ethylene polymer having a tensile modulus of less than about 2,000 psi and a crystallinity of less than about 10 percent.

3. A process as defined in claim 2 wherein said polymer has a density of about 0.89 to about 0.91 gram per cc and a pore volume of about 0.2 to about 0.4 cc per gram.

4. A process as defined in claim 2 wherein the chlorinating agent is gaseous chlorine.

5. A process as defined in claim 2 wherein the polymer is a polymer of ethylene and butene-1.

6. A process as defined in claim 2 carried out at a temperature of about 50°C to about 130°C.

7. A process as defined in claim 2 wherein the ethylene polymer has the following properties:

an average particle size of about 200 to about 1,500,

a bulk density of about 10 to about 30,

a pore volume of about 0.1 to about 1, and

a density of about 0.87 to about 0.92.

8. A granular, chlorinated ethylene polymer prepared as defined in claim 1.

9. A granular, chlorinated polymer of ethylene and at least one C_3 to C_8 alpha olefin, prepared as defined in claim 1.

10. A granular, chlorinated polymer of ethylene and butene-1, prepared as defined in claim 1.

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EUROPEAN SEARCH REPORT

0131937
Application number

EP 84 10 8259

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl ³)
Y	US-A-4 029 862 (G.Y.T. LIU) * Claims 1,2 *	1-10	C 08 F 8/20
Y	FR-A-2 381 069 (STAMICARBON) * Claim 1 *	1-10	
Y	EP-A-0 004 647 (UCC) * Page 8, line 34 - page 12, line 19 *	1-10	

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

C 08 F 8

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	12-10-1984	PERMENTIER W.A.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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